



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.04.2020 Bulletin 2020/15

(51) Int Cl.:
C09D 11/101 (2014.01) C09D 11/38 (2014.01)

(21) Application number: **19200662.5**

(22) Date of filing: **30.09.2019**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **02.10.2018 US 201862740280 P**
26.11.2018 US 201816200474

(71) Applicant: **Xerox Corporation**
Webster, NY 14580 (US)

(72) Inventors:
• **CHOPRA, Naveen**
Oakville, Ontario L6H 5W4 (CA)
• **VELLA, Sarah J.**
Milton, Ontario L9T 8E1 (CA)
• **ABRAHAM, Biby Esther**
Toronto, Ontario L5M 7E2 (CA)
• **VONG, Cuong**
Hamilton, Ontario L9C 3H5 (CA)

(74) Representative: **Gill Jennings & Every LLP**
JWF
The Broadgate Tower
20 Primrose Street
London EC2A 2ES (GB)

(54) **DIELECTRIC INK COMPOSITION**

(57) A dielectric ink composition includes at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof; a sensitizing photoin-

itiator; an amine synergist photoinitiator; a phosphine oxide photoinitiator and a gellant. A device including a dielectric layer formed by printing the dielectric ink composition described herein is also disclosed

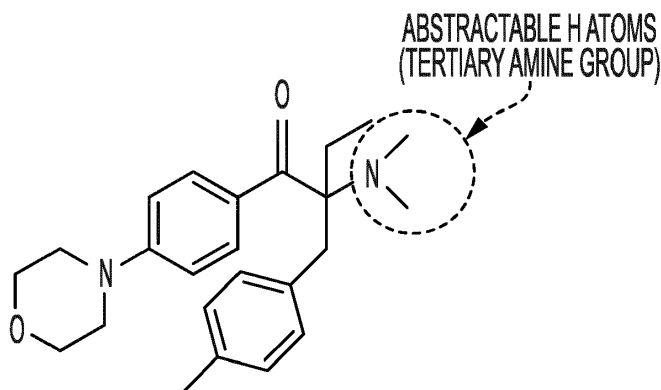


FIG. 2

Description

[0001] The present disclosure is directed to a dielectric ink composition and a device formed using the dielectric ink composition.

[0002] Printed electronics technology is an approach for the manufacturing of electronic devices using conductive inks. Complex printed electronic device architectures, such as antennae, chip interconnects and other device elements, often include insulating dielectric layers to enable 'crossovers' where two printed wires cross without making electrical contact with one another.

[0003] UV-curable compositions are an attractive option for printable dielectric materials due to possible advantages, such as 100% solids, fast cure, and customizable properties of the final polymer. One challenge to overcome when employing these UV-curable compositions is surface cure inhibition, which arises due to reaction of the monomer radicals with oxygen to create 'dead' hydroperoxy groups (R-O-O-H), thereby effectively consuming the photoinitiator at the surface, as shown in FIG. 1. The result is a sticky, uncured surface, which can have a detrimental effect on conductive ink lines printed on the dielectric surface.

[0004] A printable UV-curable dielectric material with adequate surface cure and that is capable of supporting the printing of conductive ink features on the surface with good conductivity would be a welcome addition in the art.

[0005] An embodiment of the present disclosure is directed to a dielectric ink composition. The dielectric ink composition comprises: at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof; a sensitizing photoinitiator; an amine synergist photoinitiator; a phosphine oxide photoinitiator and a gellant.

[0006] An embodiment of the present disclosure is directed to a device. The device comprises: a substrate; a first conductive line disposed over the substrate; and a second conductive line disposed over the first conductive line at a junction. A dielectric layer is disposed at the junction between the first conductive line and the second conductive line so as to electrically insulate the first conductive line from the second conductive line. The dielectric layer is formed by printing a dielectric ink composition, the dielectric ink composition comprising: at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof; a sensitizing photoinitiator; an amine synergist photoinitiator; a phosphine oxide photoinitiator and a gellant.

FIG. 1 shows a dielectric composition with a surface that is only partially cured by UV radiation due to a known problem of surface cure inhibition.

FIG. 2 shows a structural formula of an amine synergist photoinitiator, according to an example of the present disclosure.

FIG. 3 shows a structural formula of a sensitizing photoinitiator, according to an example of the present disclosure.

FIG. 4A illustrates a cross-sectional view of a dielectric layer disposed at a junction between a first conductive line and a second conductive line, according to an embodiment of the present disclosure.

FIG. 4B illustrates a perspective view of a dielectric layer disposed at a junction between a first conductive line and a second conductive line, according to an embodiment of the present disclosure.

FIG. 5 shows a graph of viscosity data for a dielectric ink composition without gellant, according to an example of the present disclosure.

FIG. 6 illustrates a microscope image of a dielectric layer with silver lines printed thereon, the dielectric layer having been made with a dielectric ink composition, according to an example of the present disclosure.

FIG. 7 illustrates microscope images of a dielectric layer with silver lines printed thereon, the dielectric layer having been made with a dielectric ink composition, according to an example of the present disclosure.

FIG. 8 illustrates a microscope image of a dielectric layer with silver lines printed thereon, the dielectric layer having been made with a comparative dielectric ink composition, according to the examples described herein.

FIG. 9 illustrates a microscope image of a dielectric layer with silver lines printed thereon, the dielectric layer having been made with a comparative dielectric ink composition, according to the examples described herein.

FIGS. 10A to 10E show a process for printing a dielectric ink composition comprising a gellant to form a dielectric layer, according to an embodiment of the present disclosure.

FIGS. 11A to 11E show a process for printing a dielectric ink composition that does not include a gellant to form a dielectric layer, according to an embodiment of the present disclosure.

FIG. 12 shows a graph of viscosity data for a dielectric ink composition comprising a gellant, according to an example of the present disclosure.

FIG. 13 illustrates a microscope image of a dielectric layer with silver lines printed thereon, the dielectric layer having been made with a dielectric ink composition, according to an example of the present disclosure.

[0007] An embodiment of the present disclosure is directed to a dielectric ink composition. The ink composition includes at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate

oligomers and combinations thereof; a sensitizing photoinitiator; an amine synergist photoinitiator; a phosphine oxide photoinitiator; and a gellant.

[0008] The curable dielectric ink composition contains at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof. The monomers include chemically reactive functionalities capable of undergoing free radical polymerization reactions with other monomers and/or the oligomers. A single species of monomer may be used or combinations of different species of monomers. Suitable, illustrative monomers include mono- and multifunctional (e.g., di-, tri-, etc.) (meth)acrylates. The term "(meth)acrylate" or "(meth)acrylates" as used herein encompasses methacrylates alone, acrylates alone or a combination of methacrylates and acrylates.

[0009] Suitable, illustrative monofunctional (meth)acrylates include 2-phenoxyethylacrylate, alkoxyated lauryl acrylate, alkoxyated phenol acrylate, alkoxyated tetrahydrofurfuryl acrylate, caprolactone acrylate, cyclic trimethylolpropane formyl acrylate, ethylene glycol methyl ether methacrylate, ethoxylated nonyl phenol acrylate, isobornyl acrylate (e.g., SR506 from Sartomer Chemical Corp.), isobornyl methacrylate (e.g., SR 423 from Sartomer Chemical Corp.), isodecyl acrylate, isooctyl acrylate, lauryl acrylate, octadecyl acrylate (stearyl acrylate), tetrahydrofurfuryl acrylate (e.g., SR285 from Sartomer Chemical Co.), tridecyl acrylate, and 4-acryloyl morpholine (from Aldrich Chemical Co.). Monofunctional urethane (meth)acrylates such as 2-[[[butylamino]carbonyl]oxy]ethyl acrylate, available from IGM Resins under the product name Photomer 4184 may also be used.

[0010] Suitable, illustrative difunctional (meth)acrylates include 1,12 dodecane diol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate (e.g., SR238B from Sartomer Chemical Co.), alkoxyated hexanediol diacrylate, alkoxyated neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, diethylene glycol diacrylate (e.g., SR230 from Sartomer Chemical Co.), ethoxylated (4) bisphenol A diacrylate (e.g., SR601 from Sartomer Chemical Co.), neopentyl glycol diacrylate, polyethylene glycol (400) diacrylate (e.g., SR344 from Sartomer Chemical Co.), propoxylated (2) neopentyl glycol diacrylate (e.g., SR9003B from Sartomer Chemical Co.), tetraethylene glycol diacrylate (e.g., SR268 from Sartomer Chemical Co.), tricyclodecane dimethanol diacrylate (e.g., SR833S from Sartomer Chemical Co.), triethylene glycol diacrylate (e.g., SR272 from Sartomer Chemical Co.), and tripropylene glycol diacrylate.

[0011] Suitable, illustrative trifunctional (meth)acrylates include ethoxylated (9) trimethylol propane triacrylate, pentaerythritol triacrylate, propoxylated (3) glyceryl triacrylate (e.g., SR9020 from Sartomer Chemical Co.), propoxylated (3) trimethylol propane triacrylate (e.g., SR492 from Sartomer Chemical Co.), and tris (2-hydroxyethyl) isocyanurate triacrylate (also referred to herein as tris (2-hydroxy ethyl acrylate) isocyanurate, available commercially as, e.g., SR368 from Sartomer Chemical Co.).

[0012] Other suitable multifunctional (meth)acrylates include ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate (e.g., SR399 from Sartomer Chemical Co.), and ethoxylated (4) pentaerythritol tetraacrylate (e.g., SR494 from Sartomer Chemical Co.).

[0013] In embodiments, the monomers include one or more, such as all three, of monofunctional (meth)acrylates, di(meth)acrylates, and tri(meth)acrylates, where di(meth)acrylates and tri(meth)acrylates are respectively referred to herein as difunctional (meth)acrylates and trifunctional (meth)acrylates. Thus, in an embodiment, the monomers can include at least one monofunctional (meth)acrylate, at least one difunctional (meth)acrylate and at least one trifunctional (meth)acrylate. In an embodiment, the compositions of the present disclosure include 2, 3, 4 or more different (meth)acrylates monomers.

[0014] In embodiments, the monomers include a tri(meth)acrylate that act as a cross-linker (e.g., a trifunctional (meth)acrylate crosslinker), such as tris (2-hydroxy ethyl acrylate) isocyanurate. The amount of trifunctional (meth)acrylate crosslinker can be any suitable amount, such as, for example, from about 2 wt. % to about 25 wt. %, such as about 5 wt. % to about 20 wt. %, or about 5 wt. % to about 15 wt. %, based on the total weight of the wet dielectric ink composition. Unless otherwise stated, all weight percentages given herein for ingredients of the dielectric ink composition are based on the total amount of wet dielectric ink composition (e.g., the composition that is ready for printing).

[0015] In embodiments, the monomers do not include tricyclodecane dimethanol diacrylate. In embodiments, the monomers do not include a non-oligomeric urethane (meth)acrylate, a urea (meth)acrylate, an isocyanurate (meth)acrylate, or all three. In embodiments, the monomers do not include tris(2-hydroxy ethyl) isocyanurate triacrylate. In embodiments, the monomers do not include a monofunctional urethane (meth)acrylate. In embodiments, the monomers do not include 2-[[[butylamino]carbonyl]oxy]ethyl acrylate.

[0016] Monomers utilized in the curable dielectric ink composition which are liquids at room temperature may be each characterized by a dynamic viscosity, as measured using a commercially available rheometer such as the Ares G2 from TA instruments. In embodiments, the monomer has a dynamic viscosity of less than about 50 cP at about 25 °C. This includes embodiments in which the monomer has a dynamic viscosity of less than about 40 cP at about 25 °C or less than about 30 cP at about 25 °C. In embodiments, the monomer has a dynamic viscosity in the range of from about 5 cP to about 50 cP at about 25 °C. This includes embodiments in which the viscosity is in the range of from about 5 cP to about 30 cP at about 25 °C or from about 5 cP to about 25 cP at about 5 °C. If more than one type of monomer is present in the curable dielectric ink compositions, these viscosity values may refer the viscosity value of each individual

monomer present in the curable dielectric ink compositions.

[0017] Monomers utilized in the curable dielectric ink composition which are solids at room temperature may be each characterized by a melting temperature. In embodiments, the monomer has a melting temperature in the range of from about 30 °C to about 100 °C. This includes embodiments in which the melting temperature is in the range of from about 30 °C to about 70 °C, or from about 40 °C to about 60 °C.

[0018] Monomers utilized in the curable dielectric ink composition may be characterized by a high glass transition temperature (T_g). For example, one or more of the monomers can have glass transition temperatures ranging from about 20°C to about 300°C, such as about 35°C to about 275°C, or about 60°C to about 200°C, or about 80°C to about 200°C. An example of a monomer with a relatively high glass transition temperature is isobornyl acrylate, which has a glass transition temperature of about 100°C. Multifunctional (meth)acrylates can have glass transition temperatures exceeding 100°C, owing to the high degree of crosslinking. An example of a multifunctional monomer with a relatively high glass transition temperature is tris-(2-hydroxyethyl acrylate) isocyanurate, with a glass transition temperature of 272°C. Other example glass transition temperatures include for various monomers/oligomers include: SR272 (triEGDA), a T_g of 47°C; S268 (tetraEGDA), a T_g of 23°C; and BR741D, a T_g of 79°C. Employing one or more monomers with relatively high glass transition temperatures can improve the toughness of any parts made from the dielectric material. This can be useful in various processes, such as where the dielectric is employed in a 3D printed part.

[0019] The monomers may be included in the present curable dielectric ink compositions in various suitable amounts. In embodiments, the monomer is present in the curable dielectric ink composition in an amount ranging from about 1 weight % to about 50 weight %, based on the total weight of the curable dielectric ink composition. This includes embodiments in which the monomer is present in an amount ranging from about 1 weight % to about 10 weight %, from about 4 weight % to about 8 weight %, from about 8 weight % to about 20 weight %, from about 20 weight % to about 45 weight %, or from about 25 weight % to about 40 weight %, based on the total weight of the curable dielectric ink composition. In embodiments in which more than one species of monomer is present in the curable dielectric ink composition, these amounts may refer to the amount of each individual monomer present in the curable dielectric ink composition.

[0020] In embodiments, the total amount of monomer present in the curable dielectric ink composition is not more than 90 weight %, based on the total weight of the curable dielectric ink composition. This includes embodiments in which the total amount is in the range of from about 35 weight % to about 80 weight %, from about 50 weight % to about 75 weight %, or from about 55 weight % to about 75 weight %, based on the total weight of the curable dielectric ink composition.

[0021] In embodiments, the curable dielectric ink composition includes at least two species of monomer having different viscosity values. The present curable dielectric ink compositions may be characterized by relatively high ratios of the lowest viscosity mono-functional or di-functional monomer to the weight % of the highest viscosity mono-functional or di-functional monomer (as determined by the (weight % of the lowest viscosity mono-functional or di-functional monomer)/(weight % of the highest viscosity mono-functional or di-functional monomer)), where the viscosity values are determined at room temperature (e.g., 25°C). In embodiments, this ratio is at least about 2. This includes embodiments in which the ratio is at least about 3, at least about 4, or at least about 5. In embodiments, this ratio is in the range of from about 2 to about 10. This includes embodiments in which the ratio is in the range of from about 3 to about 9, or about 4 to about 9, or from about 5 to about 8. As an example calculation, the mono- and di- functional monomers in the formulations of Table 1 of the present application include isobornyl acrylate (viscosity of about 8 cps); triethylene glycol diacrylate (viscosity of about 15 cps) and tetraethylene glycol diacrylate (viscosity of about 20 cps). Thus, for the formulation of Example 4 of Table 1, the weight ratio of the lowest viscosity mono-functional or di-functional monomer to the weight % of the highest viscosity mono-functional or di-functional monomer would be the weight % of isobornyl acrylate (37.6 wt.%) divided by the weight % of tetraethylene glycol diacrylate (6.8 wt.%), which is a ratio of about 5.5.

[0022] In an embodiment, the curable dielectric ink composition contains at least one (meth)acrylate oligomer. A single species of oligomer may be used or combinations of different species of oligomers. Suitable, illustrative (meth)acrylate oligomers include polyester (meth)acrylate oligomers, polyether (meth)acrylate oligomers, epoxy (meth)acrylate oligomers, and urethane (meth)acrylate oligomers. Regarding urethane (meth)acrylate oligomers, known methods may be used to prepare the compounds, such as by reacting a hydroxyl-terminated urethane compound with (meth)acrylic acid or by reacting an isocyanate-terminated compound with hydroxyalkyl (meth)acrylates. The oligomers may be characterized by their functionality, depending upon the degree of branching within the molecule. In embodiments, the oligomers utilized in the curable dielectric ink composition include difunctional compounds, trifunctional compounds, tetrafunctional compounds, pentafunctional compounds, hexafunctional compounds, or combinations thereof.

[0023] The oligomers utilized in the curable dielectric ink composition may each be characterized by a dynamic viscosity, as measured using a commercially available rheometer such as the Ares G2 from TA instruments. In embodiments, the oligomer has a viscosity in the range of from about 10,000 cP to about 200,000 cP at about 50 °C. This includes embodiments in which the viscosity is in the range of from about 15,000 cP to about 35,000 cP at about 50 °C or from about 100,000 cP to about 200,000 cP at about 50 °C. In embodiments, the oligomer has a viscosity in the range of

from about 1,000 cP to about 20,000 cP at about 25 °C. This includes embodiments in which the viscosity is in the range of from about 1,000 cP to about 15,000 cP at about 25 °C or from about 5,000 cP to about 10,000 cP at about 25 °C. If more than one type of oligomer is present in the curable dielectric ink compositions, these viscosity values may refer to the viscosity values for each individual oligomer present in the curable dielectric ink composition.

[0024] The oligomers utilized in the curable dielectric ink composition may each be characterized by a glass transition temperature, T_g , as measured using modulated differential scanning calorimetry on a commercially available differential scanning calorimeter (e.g., Discovery DSC 2500 from TA Instruments). In embodiments, the T_g is less than about 300 °C, in embodiments less than about 200 °C or less than about 100 °C. This includes embodiments in which the T_g is in the range of from about 50 °C to about 300 °C, from about 60 °C to about 200 °C, or from about 60 °C to about 100 °C. If more than one type of oligomer is present in the curable dielectric ink compositions, these T_g values may refer to the T_g values for each individual oligomer present in the curable dielectric ink composition.

[0025] Suitable, illustrative polyester (meth)acrylate oligomers include those commercially available from Sartomer Chemical Co. under the product names CN293, CN299, CN292, CN296, CN2279, CN2262, CN2267, CN2200, CN2203, and CN2281.

[0026] Suitable, illustrative polyether (meth)acrylate oligomers include those commercially available from Rahn Corp. under the product names Genomer 3364, Genomer 3414, Genomer 3457, and Genomer 3497.

[0027] Suitable, illustrative epoxy (meth)acrylate oligomers include those commercially available from Sartomer Chemical Co. under the product names CN104Z, CN2102E, CN110, CN120Z, CN116, CN117, CN118, CN119, and CN2003B or commercially available from Rahn Corp. under the product names Genomer 2235, Genomer 2252, Genomer 2253, Genomer 2255, Genomer 2259, Genomer 2263, Genomer 2280, and Genomer 2281.

[0028] Suitable, illustrative urethane (meth)acrylate oligomers include aromatic urethane (meth)acrylates such as those commercially available from Sartomer Chemical Co. under the product names CN9782, CN9783, CN992, CN975 (hexafunctional), and CN972, or commercially available from Rahn Corp. under the product names Genomer 4622 and Genomer 4217. Aliphatic urethane (meth)acrylates include those commercially available from Sartomer Chemical Co. under the product names CN9004, CN9005, CN9006, CN9023, CN9028, CN9178, CN969, CN9788, CN986, CN989, CN9893, CN996, CN2920, CN3211, CN9001, CN9009, CN9010, CN9011, CN9071, CN9070, CN929, CN962, CN9025, CN9026, CN968, CN965, CN964, CN991, CN980, CN981, CN983, CN9029, CN9030, CN9031, CN9032, CN9039, CN9018, CN9024 and CN9013 or commercially available from Rahn Corp. under the product names Genomer 4188, Genomer 4215, Genomer 4230, Genomer 4267, Genomer 4269, Genomer 4312, Genomer 4316, Genomer 4425, Genomer 4590 and Genomer 4690. Other examples include difunctional urethane methacrylate oligomers commercially available from Sartomer Chemical Co. under the product names CN1963 and CN1964.

[0029] Other suitable, illustrative urethane (meth)acrylate oligomers include the Bomar™ series of polyester urethane acrylate oligomers commercially available from Dymax Corporation under the product names: BR-441B, BR-471, BR704P, BR-741, BR-741D (a difunctional aliphatic polyester urethane acrylate oligomer), BR-742P, BR-7432GI30, BR-744BT, BR742M, BR-941, BR-952, BR-952D, BR-116, BR-146 and BR-202. Other examples include the difunctional polyester urethane methacrylate oligomer commercially available from Dymax Corporation under the product name Bomar™ XR-741MS.

[0030] Trifunctional urethane (meth)acrylate oligomers such as those commercially available from IGM Resins under the following product names may also be used: Photomer 6008, Photomer 6010, Photomer 6019, Photomer 6184, Photomer 6630, and Photomer 6892.

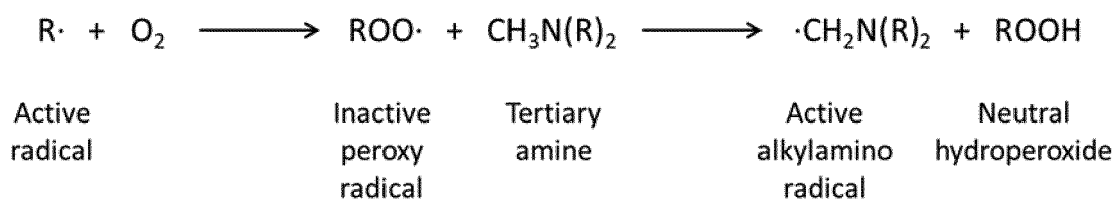
[0031] In embodiments, the curable dielectric ink composition includes greater than 10 weight % of the oligomer, based on the total weight of the curable dielectric ink composition. This includes embodiments in which the curable dielectric ink composition includes about 10 weight % to about 75 weight %, such as about 15 weight % to about 50 weight %, or about 15 weight % to about 30 weight %, or about 17 weight % to about 25 weight %, of the oligomer, based on the total weight of the curable dielectric ink composition. The maximum amount of oligomer depends upon the selected oligomer(s), but will generally be the amount at which it is still possible to jet the curable dielectric ink composition at the selected jetting temperature (e.g., about 85 °C) or at a maximum jetting temperature. In embodiments, the maximum amount of oligomer is about 75 weight %, based on the total weight of the curable dielectric ink composition. In embodiments, the curable dielectric ink composition includes from greater than about 50 weight % to 75 weight % of the oligomer. In embodiments in which more than one species of oligomer is present in the curable dielectric ink composition, these amounts refer to the total amount of oligomer in the curable dielectric ink composition.

[0032] The present curable dielectric ink compositions may be characterized by the ratio of oligomer to monomer (as determined by the (weight % of total oligomer)/(weight % of total monomer)). In embodiments, this ratio is at least about 0.2. This includes embodiments in which this ratio is about 0.2 to about 1.5, such as about 0.2 to about 1, or about 0.2 to about 0.7 or about 0.25 to about 0.5. The present curable dielectric ink compositions may also be characterized by the ratio of the sum of the weight percent of trifunctional monomers to the sum of the weight percent of all other monomers (as determined by the (weight % of total trifunctional monomers)/(weight % of total non-trifunctional monomers)). In embodiments, this ratio of trifunctional monomer to total sum of all non-trifunctional monomers ranges from about 1:8

to about 1:4., such as about 1.2:8 to about 1:5, or about 1.4:8 to about 1:5.

[0033] The compositions of the present disclosure employ an amine synergist photoinitiator. Suitable amine synergist photoinitiators are photoactive organic compounds that include a tertiary amine group that can donate a hydrogen atom to a peroxy radical. An example of a suitable amine synergist photoinitiator is 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one, which is commercially available as Irgacure 379, available from BASF of Florham Park, NJ. FIG. 2 shows the structure of 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one, with the tertiary amine group encircled with a dashed line. Another example of a suitable amine synergist is Ethyl Michler's ketone (EMK). Examples of suitable commercially available amine synergist photoinitiators include oligoamines from Rahn such as Genomer 514, Genomer 5161, Genomer 5271, and Genomer 5275; amines such as Genocure MDEA, Genocure EMK, Genocure EHA, Genocure EPD; polymeric amine synergists such as Genopol AB-2. Other amine synergist examples from Sartomer include aminated acrylates such as CN371 and CN3715, CN3755. Other examples from IGM resins include Omnipol ASA (a polymeric amine), Esacure A 198 (difunctional amine synergist), Omnirad EDB, Omnirad EHA, Omnirad IADB, Omnirad 369 and Omnirad 379. Combinations of any of the above amine synergist photoinitiators can be employed.

[0034] A potential mechanism for how the amine synergist photoinitiators function to scavenge oxygen is shown in Scheme 1, below.



(Scheme 1)

During UV curing of the dielectric films of the present disclosure, active radicals are formed, such as when a photoinitiator is activated with UV radiation or when an activated photoinitiator reacts with another compound, such as a monomer or oligomer. The active radicals can undesirably react with oxygen near the surface of the dielectric film, thereby forming peroxy radicals and in the process converting the active radical to an inactive peroxy radical. This is undesirable because the inactive peroxy radical is unable to promote the polymerization reaction, thereby resulting in inefficient and/or insufficient curing. However, the amine synergist photoinitiators of the present disclosure are able to donate a hydrogen atom to the inactive peroxy radical, and in the process form an active alkylamino radical, as shown in Scheme 1. The resulting active alkylamino radical is highly reactive, and is thereby able to promote the polymerization reaction of the (meth)acrylate compounds employed in the dielectric ink composition. Further, the active alkylamino radical is unaffected by oxygen at the surface of the dielectric film, thereby enabling adequate curing of the dielectric film at the surface.

[0035] The amount of amine synergist photoinitiator employed in the dielectric ink compositions can be any suitable amount that provides for the desired curing at the surface of the resulting dielectric film. As an example, the amount of amine synergist photoinitiator can range from about 0.5 wt. % to about 10 wt. %, such as about 1.5 wt. % to about 7.5 wt. %, or about 3 wt. % to about 6 wt. %, or about 3 wt. % to about 4.5 wt. %, based on the total weight of the wet dielectric ink composition.

[0036] The sensitizing photoinitiators are employed to harvest the long wavelength UV light that is employed for the curing process and to transfer energy to the photoinitiators. The particular sensitizing photoinitiator used can depend on the wavelength of UV light used for curing. In an embodiment, the sensitizing photoinitiator absorbs UV radiation in a range of about 270 nm to about 410 nm, thereby forming an excited photoinitiator (also referred to herein as an "excited triplet sensitizer"). The excited triplet sensitizer can, in turn, pass its triplet energy to the amine synergist photoinitiator and/or other photoinitiators used in the dielectric ink composition.

[0037] Any suitable sensitizing photoinitiator can be employed that can absorb UV light at the wavelength of light used for curing, and transfer the energy to other photoinitiators in the dielectric ink composition to enable the generation of free radicals so as to initiate the polymerization process. An example of a suitable sensitizing photoinitiator is 2-isopropyl thioxanthone, which is a thioxanthone photoinitiator commercially available as Darocure ITX from BASF of Florham Park, NJ. FIG. 3 shows the structure of 2-isopropyl thioxanthone. Examples of other suitable sensitizing photoinitiators include thioxanthenes such as 2,4-diethylthioxanthone (DETX), 2-chlorothioxanthone (CTX), 2,4-dimethylthioxanthone (RTX) and 1-chloro-4-propoxythioxanthone (CPTX). Other examples of commercially available sensitizers include: Rahn Corporation (Genopol TX-2 (polymeric thioxanthone), Genocure ITX, Genocure DETX. IGM Resins (Omnipol TX, Omnipol 3TX, Omnipol BL728, all polymeric); Omnirad ITX, Omnirad DETX. Lambson Group Ltd: Speedcure ITX, Speedcure 2-ITX, Speedcure 7010 (a CPTX), Speedcure 7010-L (polymeric).

[0038] The amount of sensitizing photoinitiator employed in the dielectric ink compositions can be any suitable amount that provides for the desired degree of polymerization to achieve adequate curing. As an example, the amount of sensitizing photoinitiator can range from about 0.5 wt. % to about 10 wt. %, such as about 1.5 wt. % to about 7.5 wt. %, or about 3 wt. % to about 6 wt. %, or about 3 wt. % to about 4.5 wt. %, based on the total weight of the wet dielectric ink composition.

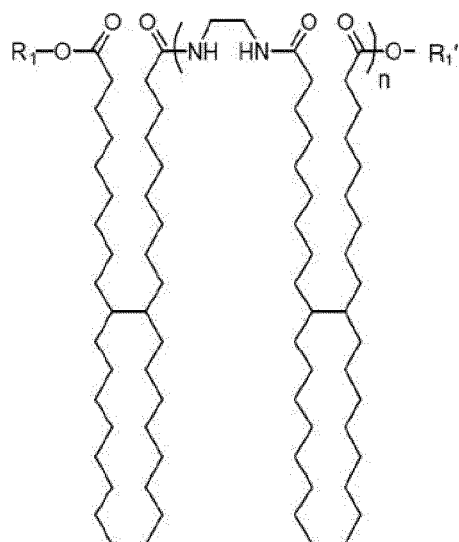
[0039] The combination of the amine synergist photoinitiator and the sensitizing photoinitiator in the dielectric composition results in the acceleration of curing and allows for the scavenging of oxygen at the surface of the dielectric layer. Thus, an adequate degree of curing can more efficiently be achieved at the surface of the dielectric layer (e.g., a complete surface cure or a substantially complete surface cure).

[0040] A phosphine oxide photoinitiator is also employed in the compositions of the present disclosure. The phosphine oxide is a long wavelength UV absorber, particularly suited for LED light and highly pigmented coatings, and is also suited for depth cure due to a high degree of penetration into the coating. An example of a suitable phosphine oxide photoinitiator is Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, which is commercially available as Irgacure 819, from BASF of Florham Park, NJ. Other suitable phosphine oxides include Diphenyl-(2,4,6, Trimethylbenzoyl)phosphine oxide (TPO) and Ethyl (2,4,6-trimethylbenzoyl)phenylphosphinate (TPO-L). Examples of commercially available phosphine oxide photoinitiators include Lucirin TPO and Lucirin TPO-L from BASF; Genocure TPO and Genocure TPO-L from Rahn AG of Zurich, Switzerland; and Omnirad TPO, Omnirad TPO-L and Omnirad 819, from IGM Resins of Charlotte, North Carolina. Combinations of any of the above phosphine oxides can be employed.

[0041] The amount of phosphine oxide photoinitiator employed in the dielectric ink compositions can be any suitable amount that provide for the desired polymerization so as to provide adequate curing. As an example, the amount of phosphine oxide photoinitiator can range from about 0.5 wt. % to about 10 wt. %, such as about 1.5 wt. % to about 7.5 wt. %, or about 3 wt. % to about 6 wt. %, or about 3 wt. % to about 4.5 wt. %, based on the total weight of the wet dielectric ink composition.

[0042] A gellant is also employed in the dielectric ink compositions of the present disclosure. The gellant functions as a phase change agent, enabling a relatively sharp increase in viscosity as the ink cools below the jetting temperature. An example of such a change in viscosity is shown in FIG. 12 and discussed in more detail in the examples below.

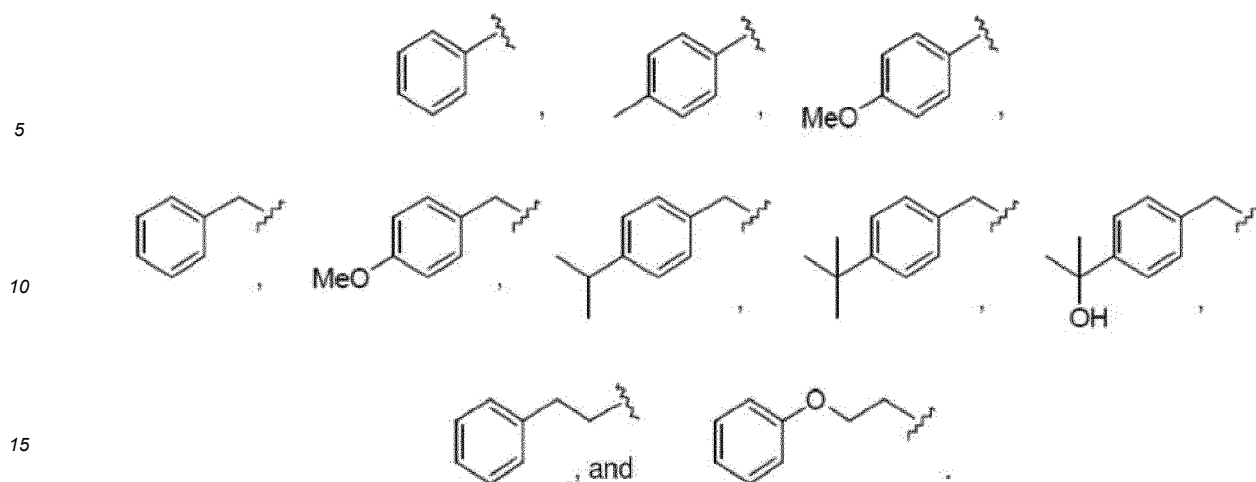
[0043] Examples of suitable gellants include amide gellants, such as ester-terminated polyamides (ETPAs), which show a relatively high degree of solubility in the (meth)acrylate containing ink compositions of the present disclosure. The ETPA gellant can comprise a blend of monomers and oligomers or "x-mers" (e.g., monomers, dimer, trimer, tetramer, pentamer, etc.) of an ester-terminated polyamide resin. The generic structure of an ETPA gellant is shown as Formula 1 below:



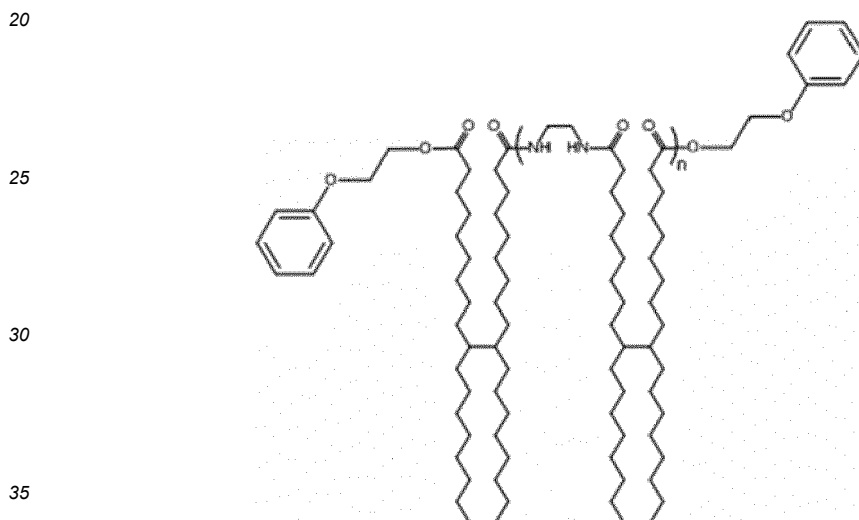
(Formula 1)

where n is about 0 to about 20, about 0 to about 15, or about 0 to about 10, and where R₁ and R₁ each, independently of the other, is a suitable end-capping group (e.g., an alcohol, aromatic, or aromatic alcohol group). In some embodiments, n is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20.

[0044] In some embodiments, R1 and R1' each, independently of the other, is an aromatic group selected from the group consisting of:



[0045] One example of suitable ETGA gellant is the compound of formula 2 below:



(Formula 2)

where n is about 0 to about 20, about 0 to about 15, or about 0 to about 10. The amide gellant compounds are available from Xerox Corporation of Stamford, Connecticut.

[0046] The phase change property imparted to the dielectric ink compositions by the gellant enables the buildup of thicker dielectric layer profiles without the need for intermediate curing steps. For example, dielectric layers having a thickness of about 0.5 micron to 5000 microns, or about 2.0 microns to 3000 microns, or about 10 microns to about 1000 microns can be formed without employing an intervening curing step. FIGS. 10A to 10E show the advantages of using the phase-change dielectric ink of the present disclosure to form a dielectric layer versus a similar process, shown in FIGS. 11A to 11E, which employs a non-phase-change dielectric ink composition. In FIG. 10A, the dielectric ink composition comprising the gellant is jetted (e.g., by ink jet or aerosol jet printing) onto a substrate 102 to form first dielectric ink layers 103. The temperature of substrate 102 can be lower than the jetting temperature dielectric ink, thereby causing the dielectric ink to cool and gel. For example, the substrate temperature can range from about 0°C to about 50°C, such as about 15°C to about 30°C, or about 20°C to about 25°C, such as room temperature. Because the gellant containing dielectric ink is relatively viscous at lower temperatures, one or more additional layers of dielectric ink composition can then be printed on the first dielectric ink layers 103 without an intervening cure step, thereby building up the thickness of dielectric ink layer 103, as shown in FIG. 10B. After the dielectric ink layer 103 reaches the desired final thickness, the dielectric ink layer 103 is exposed to UV radiation to cure the ink and form dielectric layer 106, as shown in FIG. 10C. One or more conductive ink lines 107 can then be printed onto the dielectric layer, following by an anneal of the conductive ink lines 107 to form conductive lines 108, as shown in FIGS. 10D and 10E. The process of FIGS. 11A to 11E is similar to the process of FIGS. 10A to 10E, except that because the process shown in FIGS. 11A to 11E employs an ink that

does not include a gellant, an intervening curing step is carried out at FIG. 11B, after the first dielectric ink layer 103 is printed, and before any additional dielectric ink layers are printed on the first dielectric ink layer to increase thickness. The process of FIGS. 11A and 11B is then repeated to build up the thickness of the dielectric layer 106 to achieve a desired final thickness as shown in FIG. 11C, with additional intervening UV cure steps occurring each time an additional layer of dielectric ink is printed. The intervening UV cure steps are employed because the dielectric ink without the gellant is not sufficiently viscous to support the additional dielectric ink layers. Thus, the process shown in FIG. 10 can perform the cure of the dielectric layer using fewer UV exposures than the process of FIG. 11. Further, the ability to employ a single cure step can mean fewer interfaces in the dielectric layer.

[0047] In an embodiment, the only photoinitiators employed in the dielectric ink compositions are the amine synergist photoinitiator, the sensitizing photoinitiator and the phosphine oxide photoinitiator. Alternatively, the dielectric ink composition can further contain one or more additional photoinitiators other than those listed above. Any photoinitiator that absorbs radiation, for example, UV or visible radiation, to induce free radical polymerization reactions between the selected oligomers and/or selected monomers may optionally be used. Suitable, illustrative optional photoinitiators such as benzophenones, benzoin ethers, benzil ketals, α -hydroxyalkylphenones, α -alkoxyalkylphenones, α -aminoalkylphenones, and acylphosphine photoinitiators may be used. The photoinitiator 2,4,6 Trimethylbenzoyldiphenylphosphine oxide (TPO) may be used. Suitable, illustrative optional photoinitiators include those commercially available from BASF under the product names Irgacure-184 and Irgacure TPO may be used.

[0048] The optional photoinitiator may be included in the curable dielectric ink composition in various suitable amounts. In embodiments, curable dielectric ink composition includes from about 0.1 weight % to about 10 weight % of the optional photoinitiator, based on the total weight of the wet dielectric ink composition. This includes embodiments in which the curable dielectric ink composition includes from about 0.1 weight % to about 8 weight % or from about 0.1 weight % to about 6 weight % of the photoinitiator based on the total weight of the wet dielectric ink composition. In embodiments in which more than one species of optional photoinitiator is present in the curable dielectric ink composition, these amounts may refer to the amount of each optional photoinitiator in the curable dielectric ink composition.

[0049] A variety of other additive ingredients may optionally be added to the dielectric ink composition. Suitable, illustrative additives include colorants, polymerization inhibitors to promote thermal stability, and antioxidant agents. When present, additives may be included in various suitable amounts. In embodiments, the curable dielectric ink composition includes from about 0.1 weight % to about 15 weight % of each of the thermal stability and/or antioxidant agents additive, based on the total weight of the curable dielectric ink composition, such as about 0.1 weight % to about 10 weight % or from about 0.1 weight % to about 5 weight % of the additive based on the total weight of the curable dielectric ink composition. In embodiments in which more than one species of additive is present in the curable dielectric ink composition, these amounts may refer to the amount of each of the additives in the curable dielectric ink composition.

[0050] The dielectric ink compositions of the present disclosure can be clear or colored. If a colorant is employed, the colorant can be chosen from a dye, a pigment or mixtures thereof. Any dye or pigment may be chosen, provided that it is capable of being dispersed or dissolved in the dielectric ink and is compatible with the ink components.

[0051] The colorant may be present in the dielectric ink composition in any desired or effective amount to obtain the desired color or hue such as, for example, from about 0.1 percent by weight of the ink to about 50 percent by weight of the ink, or from about 0.2 percent by weight of the ink to about 20 percent by weight of the ink, or from about 0.5 percent by weight of the ink to about 10 percent by weight of the wet dielectric ink composition.

[0052] Any other ingredients suitable for use in printable inks, such as, for example, solvents, can also optionally be included in the compositions of the present disclosure. One of ordinary skill in the art would readily be able to determine other ingredients that can be employed.

[0053] The ink compositions can be prepared by any desired or suitable method. For example, various curable dielectric ink compositions may be formed according to the guidance provided above, for example, curable dielectric ink compositions having various combinations of the disclosed components at the disclosed amounts and ratios. Such curable dielectric ink compositions may have (in uncured and uncured forms) various combinations of the characteristics disclosed throughout this specification. In embodiments, the curable dielectric ink compositions consist or consist essentially of the disclosed components, i.e., the oligomer component, the monomer component, the photoinitiator component, and optionally, the additive component.

[0054] The curable dielectric ink compositions may be formed by combining the selected components at the selected amounts under conditions sufficient to form a homogeneous liquid mixture. Illustrative methods are described in the Examples, below.

[0055] The dielectric ink composition prior to curing (sometimes referred to herein as the "wet dielectric ink composition") may be characterized by a complex viscosity that is suitable for jetting using an ink jet printer or aerosol printer. These viscosity values may be referred to as "jettable viscosity values" in that curable dielectric ink compositions having such viscosity values are able to be jetted by various digital additive manufacturing systems at typical jetting temperatures (e.g., 85 °C). For example, the wet ink composition can have a complex viscosity of about 2 cps to about 20 cps, such as about 5 cps to 15 cps, or about 5 cps to 10 cps, at 85°C. The viscosity can be obtained by measuring complex

viscosities over a 100°C to 25°C temperature range using an Ares G2 rheometer equipped with a 25 mm Parallel plate and Peltier heating system. Samples of the inks are loaded on the rheometer at about 102°C, allowed to equilibrate, then swept over the temperature range from about 100°C to 25°C at a rate of 1.5 °C/min at 10 rad/s. The wet dielectric ink composition has a complex viscosity of greater than 1×10^4 cps, such as a viscosity ranging from about 1×10^4 cps to about 1×10^6 cps, or about 1×10^4 cps to about 1×10^5 cps, at room temperature (e.g., 25°C).

[0056] Referring to FIGS. 4A and 4B, the present disclosure is also directed to a device 100 comprising a substrate 102. A first conductive line 104 is disposed over the substrate 102. A second conductive line 108 is disposed over the first conductive line 104 at a junction 110. A dielectric layer 106 is disposed at the junction 110 between the first conductive line 104 and the second conductive line 108, so as to electrically insulate the conductive lines 104, 108 from each other. The dielectric layer 106 is formed by printing any of the dielectric ink compositions described herein.

[0057] The substrate 102 can be any desired substrate on which the dielectric inks of the present disclosure can be printed. Example substrates 102 include paper products, such as cardboard or copy paper, fabrics, textile products, plastics, polymeric films, inorganic recording mediums such as ceramics, inorganic dielectric materials (e.g., silicon dioxide), semiconductors, metals, wood, circuit boards, partially or fully fabricated electronic devices such as transistors, and the like.

[0058] In an embodiment, the dielectric layer 106 (sometimes referred to herein as a "dielectric film") can be printed only over the portion of conductive line 104 and/or portions of the substrate in proximity to the junction 110. Alternatively, the dielectric layer 106 can be formed over the entire conductive line 104 and/or the entire substrate 102. The thickness of the dielectric layer 106 can be any thickness that will provide the desired electrical insulation between the conductive lines. For example, the thickness of the dielectric layer 106 can range from about 50 nm to about 1 millimeter or more, such as about 100 nm to about 500 microns or about 200 nm to about 100 microns.

[0059] The dielectric layer 106 can be deposited by any printing techniques suitable for printing dielectric inks, including inkjet printing and aerosol jet printing. Any suitable printing device may be used for printing the dielectric inks. The phrase "printing device" as used herein encompasses any apparatus, such as a 3D printer, inkjet printer, aerosol jet printer, digital copier, bookmaking machine, facsimile machine, multi-function machine, and the like, which can jet ink to perform a print outputting function for any purpose.

[0060] The dielectric layer 106 can be cured using any suitable ultraviolet light source at any suitable UV wavelength. In an example, the light source is an LED emitting UV radiation at about 395 nm.

[0061] Dielectric layers made using the dielectric ink compositions comprising the amine synergist and sensitizing photoinitiators of the present disclosure can be cured more quickly, potentially in fewer passes (e.g., a single pass) of a UV LED light source, compared to dielectric layers made using the same dielectric ink compositions except that other photoinitiators (e.g., the photoinitiators of the Comparative Example in Table 6 below) are employed without the amine synergist and sensitizing photoinitiators of the present disclosure.

Examples 1 to 35: Ink Compositions

[0062] *General Procedure:* one or both of the following small scale or large scale procedures were used to prepare compositions as shown in the examples of Tables 1 to 6 below. Tables 1 to 5 summarize example formulations according to the present disclosure. A comparative example is shown in Table 6. All percentages are by weight relative to the total weight of the dielectric ink composition. Examples 1-9, 11-15, and 17-31 were prepared using the small scale preparation procedures (A). Examples 32-35 were prepared using the large scale procedures (B). Examples 10 and 16 were prepared using both small and large scale procedures.

- *A) Small Scale Preparation Procedure:* To an amber glass 30mL bottle was added the components in the percentages shown in the tables below, along with a magnetic stir bar. The bottle was transferred to a Vario-Mag thermowell set to 80°C with stirring at 350RPM. After 30 minutes, the ink was removed from the heater/stirrer.
- *B) Large scale (>20mL) Preparation Procedure:* A glass beaker was fitted to a jacketed heating mantle, and heated to 80°C. Next, an overhead mixer with a 4-bladed impeller was immersed, and the various components were added to the beaker. The mixture was heated for 30 minutes with mixing at 300RPM until all the solid components were completely dissolved, and the mixture was a clear, homogenous liquid. Finally, the material was passed through a 1µm Parker filter under pressure to furnish the final ink composition.

Examples 1 to 35: Ink Compositions Without A Gel

[0063] The ink compositions of Examples 1 to 35 (shown in Tables 1 to 5), while not containing a gel, do include the photoinitiators of the present disclosure, and are therefore described herein to show certain advantages of the photoinitiator systems of the present disclosure.

Table 1. Example Dielectric Ink Compositions

Preparation
Procedure

5	Component	Compound Name	Description	A	A	A	A
				Ex.1	Ex.2	Ex.3	Ex.4
	SR506A	isobornyl acrylate	Monomer	33.2%	31.2%	27.1%	37.6%
	SR272	triethylene glycol diacrylate	Monomer	13.6%	12.7%	11.1%	15.0%
	SR268	tetraethylene glycol diacrylate	Monomer	6.2%	5.8%	5.1%	6.8%
10		tris(2-hydroxy ethyl acrylate)					
	SR368	isocyanurate	Monomer	10.1%	9.5%	8.2%	11.2%
		difunctional aliphatic urethane					
	BR741D	oligomer	Oligomer	18.4%	17.3%	15.0%	20.3%
		difunctional aliphatic urethane					
15	BR952	oligomer	Oligomer				
		Phenylbis(2,4,6-trimethylbenzoyl)					
	Irgacure 819	phosphine oxide	Photoinitiator	4.5%	4.5%	4.5%	3.0%
	Darocur ITX	2-isopropyl thioxanthone	Photoinitiator	4.5%	4.5%	4.5%	3.0%
20		2-(4-methylbenzyl)-					
		2-(dimethylamino)-1-(4-					
	Irgacure 379	morpholinophenyl)butan-1-one	Photoinitiator	4.5%	4.5%	4.5%	3.0%
	Ethyl						
	Michler's						
25	Ketone	1-Hydroxycyclohexyl phenyl ketone	Photoinitiator				
	20% pigment						
	dispersion	Diphenyl(2,4,6-trimethylbenzoyl)					
	(cyan)	phosphine oxide	Colourant	5.0%	10.0%	20.0%	
	TOTAL			100.0%	100.0%	100.0%	100.0%

Table 2. Example Dielectric Ink Compositions

Preparation Procedure Component	A		A		A		A and B		A		A		A	
	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13					
SR506A	33.4%	29.7%	35.9%	35.9%	38.9%	35.2%	42.2%	37.0%	33.4%					
SR272	13.7%	12.2%	14.7%	14.7%	15.9%	14.4%	15.00%	15.2%	13.7%					
SR268	6.2%	5.6%	6.7%	6.7%	7.3%	6.6%	6.80%	6.9%	6.2%					
SR368	10.2%	9.1%	10.9%	10.9%	11.9%	10.7%	11.20%	11.3%	10.2%					
BR741D	18.5%	16.5%	19.9%	19.9%	21.6%	19.5%	20.30%	20.6%	18.5%					
BR952														
Irgacure 819	6.0%	9.0%	6.0%	6.0%	1.5%	4.5%	1.50%	3.0%	6.0%					
Darocur ITX	6.0%	9.0%	6.0%		1.5%	4.5%	1.50%	3.0%	6.0%					
Irgacure 379	6.0%	9.0%		6.0%	1.5%	4.5%								
Ethyl Michler's Ketone 20% pigment dispersion (cyan)							1.50%	3.0%	6.0%					
TOTAL	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%					

Table 3. Example Dielectric Ink Compositions

Preparation Procedure Component	A		A and B		A		A		A		A		A	
	Ex.14	Ex.15	Ex.16	Ex.17	Ex.18	Ex.19	Ex.20	Ex.21	Ex.22					
SR506A	37.7%	37.1%	37.7%	37.1%	36.5%	37.1%	36.5%	37.1%	36.5%					
SR272	15.4%	15.2%	15.4%	15.2%	14.9%	15.2%	14.9%	15.2%	14.9%					
SR268	7.0%	6.9%	7.0%	6.9%	6.8%	6.9%	6.8%	6.9%	6.8%					
SR368	11.5%	11.3%	11.5%	11.3%	11.1%	11.3%	11.1%	11.3%	11.1%					
BR741D	20.9%	20.6%	20.9%	20.6%	20.2%	20.6%	20.2%	20.6%	20.2%					
BR952														
Irgacure 819	1.5%	1.5%	1.5%	1.5%	1.5%	3.0%	3.0%	3.0%	3.0%					
Darocur ITX	1.5%	3.0%	4.5%	4.5%	4.5%	1.5%	3.0%	4.5%	4.5%					
Irgacure 379	4.5%	4.5%	1.5%	3.0%	4.5%	4.5%	4.5%	1.5%	3.0%					
Ethyl Michler's Ketone 20% pigment dispersion (cyan)														
TOTAL	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%					

Table 4. Example Dielectric Ink Compositions

Preparation Procedure Component	A		A		A		A		A		A		A		A	
	Ex.23	Ex.24	Ex.25	Ex.26	Ex.27	Ex.28	Ex.29	Ex.30	Ex.31							
SR506A	35.9%	37.7%	37.1%	36.5%	37.1%	36.5%	35.9%	36.5%	35.9%							
SR272	14.7%	15.4%	15.2%	14.9%	15.2%	14.9%	14.7%	14.9%	14.7%							
SR268	6.7%	7.0%	6.9%	6.8%	6.9%	6.8%	6.7%	6.8%	6.7%							
SR368	10.9%	11.5%	11.3%	11.1%	11.3%	11.1%	10.9%	11.1%	10.9%							
BR741D	19.9%	20.9%	20.6%	20.2%	20.6%	20.2%	19.9%	20.2%	19.9%							
BR952																
Irgacure 819	3.0%	4.5%	4.5%	4.5%	4.5%	4.5%	4.5%	4.5%	4.5%							
Darocur ITX	4.5%	1.5%	1.5%	1.5%	3.0%	3.0%	3.0%	4.5%	4.5%							
Irgacure 379	4.5%	1.5%	3.0%	4.5%	1.5%	3.0%	4.5%	1.5%	3.0%							
Ethyl Michler's Ketone 20% pigment dispersion (cyan)																
TOTAL	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%							

Table 5. Example Dielectric Ink Compositions

Preparation Procedure		B	B	B	B
Component		Ex.32	Ex.33	Ex.34	Ex.35
SR506A		35.2%	31.2%	33.4%	32.2%
SR272		14.4%	12.8%	13.7%	13.8%
SR268		6.6%	5.8%	6.2%	6.8%
SR368		10.7%	9.5%	10.2%	10.5%
BR741D			17.3%	18.6%	18.3%
BR952		19.6%			
Irgacure 819		4.5%	4.5%	4.3%	4.5%
Darocur ITX		4.5%	4.5%	4.3%	4.5%
Irgacure 379		4.5%	4.5%	4.3%	4.5%
Ethyl Michler's Ketone 20% pigment dispersion (cyan)			10.0%	5.0%	5%
TOTAL		100.0%	100.0%	100.0%	100.0%

Table 6. Comparative Dielectric Ink Compositions

Preparation Procedure		A and B	
Material	Compound name	Description	Comparative Example
			Wt%
SR506A	isobornyl acrylate	monomer	39.4%
SR272	triethylene glycol diacrylate	monomer	16.2%
SR268	tetraethylene glycol diacrylate	monomer	7.4%
SR368	tris (2-hydroxy ethyl acrylate) isocyanurate	monomer	12.0%
BR741D	difunctional aliphatic urethane oligomer	oligomer	21.8%
Irgacure 819	Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	photoinitiator	-
Darocure ITX	2-isopropyl thioxanthone	photoinitiator (sensitizer)	-
Irgacure 379	2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one	photoinitiator	-
Irgacure 184	1-Hydroxycyclohexyl phenyl ketone	photoinitiator	2.3%
Lucirin TPO	Diphenyl(2,4,6-trimethylbenzoyl)phosphine	photoinitiator	1.0%
TOTAL			100.0%

Dielectric Ink Characterization:

[0064] The viscosity of the ink of Example 10 (Table 2) was measured by performing a temperature sweep test ranging from high temperature to low temperature. In particular, the viscosity was obtained by measuring complex viscosities over a 100°C to 25°C temperature range using an Ares G2 rheometer equipped with a 25 mm Parallel plate and Peltier heating system. Samples of the inks are loaded on the rheometer at 102°C, allowed to equilibrate, then swept over the temperature range to 25°C at a rate of 1.5 °C/min at 10 rad/s. The results are shown in FIG. 5.

Dielectric properties of UV curable Dielectric Ink

[0065] The capacitance of the UV curable dielectric material made using the ink of Example 10 was measured to be about 5.25 nF/cm² and the dielectric constant was calculated to be about 3.90.

Example 36: Dielectric Ink Coating and Overprinting with Conductive Ink

[0066] A square gap coater with a 1 mil gap was used to draw down a thin film of dielectric ink of Example 10 on a precleaned 2"x3" microscope slide. The ink film was then cured under a Phoseon 12W UV LED by keeping the lamp

stationary under the UV light source for 5 seconds, at a gap of 6 centimetres. A nanoparticle-based silver ink was overprinted on top of the cured ink film using a Dimatix DMP2800 printer. The silver ink printing was carried out as follows: ink was jetted at room temperature at a print speed of 5m/sec, and the drop mass was 7ng. A standard test pattern was printed directly onto the cured dielectric film coating on glass, and then thermally annealed in an oven at 120°C for 30 minutes.

Example 37: Dielectric Ink Coating on PET substrate and Overprinting with Conductive Ink

[0067] A square gap coater with a 1 mil gap was used to draw down coat a thin film of dielectric ink of Example 10 on precleaned PET substrates. The films were cured under a Phoseon 16W UV LED lamp with the substrate moving on a belt with speeds ranging from 190.5 mm/s to 381 mm/sec, (energy densities ranging from 1152 mJ/cm² to 576 mJ/cm² and power of 10.1 W/cm²).

[0068] Silver nanoparticle (AgNP) ink was printed using a Xerox printhead on an in-house inkjet printer with the platen heated to 70°C. The AgNP ink printed excellent lines. The AgNP ink was sintered using a Novacentrix Pulseforge 1200 using the following settings: 400 V, envelope 4000 μ s, 10 μ pulses, a duty cycle of 50% which gave an energy of 4.12 J/cm².

Electrical Testing:

[0069] The photosintered silver lines of Example 37 were assed for conductivity by measuring the resistance of an 8 pixel line. The average resistance measured $\sim 8 \Omega$. The dimensions of the lines were roughly: length -50 mm, height $\sim 2.8 \mu$ m, width $\sim 408 \mu$ m, to give a calculated bulk conductivity of $\sim 9 \times 10^4$ S/cm.

[0070] Improved nanoAg line printability was demonstrated with an improved UV LED surface cure of the inventive dielectric ink material. No evidence of uncured surface residue was seen, whereas lines printed with the ink of the Comparative Example (Table 6) were sticky and smeared when rubbed. FIGS. 6 to 9 illustrate these comparisons. In particular, FIGS. 6 and 7 illustrate microscope images of a dielectric made with the ink of Example 10 (without gel), with silver ink lines printed thereon. FIGS. 8 and 9 illustrate microscope images of a dielectric made with the ink of the Comparative Example, with silver ink lines printed thereon. The silver ink lines printed on the dielectric made with the dielectric ink of Example 10 show improved uniformity and continuity. In summary, the dielectric made with the ink of Example 10 was a fully cured, tack-free film that was shown to support overprinting of conductive silver ink.

[0071] While the ink of Example 10 does not contain a gellant, it does contain a similar photoinitiator system to the gellant containing formulations of the present disclosure. Further, the gellant containing dielectric inks of the present disclosure have been shown to result in overprinted conductive lines of similar quality when compared to the ink of Example 10, as shown in Example 39 below and FIG. 13. Therefore, the above test results for the Examples made without gel taken together with the Examples employing a gel below, provide evidence of the advantages of using the photoinitiators of the present disclosure in dielectric inks made with or without a gellant.

Example 38: Large Scale Dielectric Ink Comprising a Gellant

[0072] The formulation of Table 7 was made as described above in the General Procedure and/or the Larger Scale procedure.

Table 7: Ink Formulation with Gellant

Material	Compound name	Description	Ex.38	
			Wt%	Mass (g)
SR506A	isobornyl acrylate	monomer	33.9%	101.7
SR272	triethylene glycol diacrylate	monomer	19.8%	59.3
SR268	tetraethylene glycol diacrylate	monomer	5.0%	15.0
SR368	tris (2-hydroxy ethyl acrylate) isocyanurate	monomer	10.1%	30.4
BR741D	difunctional aliphatic urethane oligomer	oligomer	12.7%	38.1
Irgacure 819	Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	photoinitiator	4.5%	13.5
Darocure ITX	2-isopropyl thioxanthone	photoinitiator (sensitizer)	4.5%	13.5

(continued)

Material	Compound name	Description	Ex.38	
			Wt%	Mass (g)
Irgacure 379	2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one	photoinitiator	4.5%	13.5
Amide gellant	Ester-Terminated Polyamide of Formula 2	phase-change material	5.0%	15.0
TOTAL			100.0%	300

Dielectric Ink Characterization

[0073] The viscosity of the ink was measured by performing a temperature sweep test ranging from high temperature to low temperature. In particular, the viscosity was obtained by measuring complex viscosities over a 100°C to 25°C temperature range using an Ares G2 rheometer equipped with a 25 mm Parallel plate and Peltier heating system. Samples of the inks were loaded on the rheometer at about 102 °C, allowed to equilibrate, then swept from about 100°C to 25°C at a rate of 1.5 °C/min at 10 rad/s. FIG. 12 shows the viscosity curve. Note the sharp increase in viscosity of the ink at lower temperatures.

Example 39: Small Scale Dielectric Ink Comprising a Gellant

[0074] The formulation of Table 8 was made as described above in the General Procedure for the Small Scale procedure.

Table 8: Ink Formulation with Gellant

Ex. 39	Wt. %	wt
SR506 A (IBOA - isobornyl acrylate)	33.4%	1.69
SR272 (TriEGDA - triethylene glycol diacrylate)	13.7%	0.69
SR268 (TetraEGDA - tetraethylene glycol diacrylate)	6.3%	0.32
SR368 (tris-2-hydroxyethylacrylate isocyanurate triacrylate)	10.2%	0.52
Bomar BR952D (aliphatic urethane diacrylate)	18.6%	0.94
Irgacure 819	4.3%	0.22
Darocure ITX	4.3%	0.22
Irgacure 379	4.3%	0.22
amide gellant	4.9%	0.25
TOTAL	100.0%	5.05

Example 40: Dielectric Ink Coating and Overprinting with Conductive Ink

[0075] A square gap coater with a 1 mil gap was used to draw down a thin film of the ink of Example 39 on a precleaned 2"x3" microscope slide. The microscope slide was kept on a hotplate at 85°C to keep the ink in a molten state. The gap coater and ink were kept in the oven just until the coating was made, again to ensure a smooth film. The ink film was cooled to room temperature, and then cured under a Phoseon 12W UV LED by keeping the lamp stationary under the UV light source for 5 seconds, at a gap of 6 centimeters.

[0076] A nanoparticle-based silver ink was overprinted on top of the cured ink film using a Dimatix DMP2800 printer. The silver ink printing was carried out as follows: ink was jetted at room temperature at a print speed of 5m/sec, and the drop mass was 7ng. A standard test pattern was printed directly onto the cured dielectric film coating on glass, and then thermally annealed in an oven at 120°C for 30 minutes. Visual inspection of both the uncured and cured silver ink lines

served as a means of assessing the quality of the dielectric coating as a printing surface for conductive ink. Smooth continuous silver lines were observed, as shown in FIG. 13.

Examples 41 to 49: Dielectric Inks Comprising a Gellant

[0077] The formulation of Tables 9 and 10 below were made as described above in the General Procedure using either the Preparation Procedure A (Small Scale), Preparation Procedure B (Large Scale) or both, as shown in the tables.

Table 9: Ink Formulation with Gellant

<i>Preparation Procedure</i>		A	A	A	B
Component	Description	Ex.41	Ex.42	Ex.43	Ex.44
SR506A	Monomer	34.7%	34.3%	32.6%	35.2%
SR272	Monomer	14.3%	14.1%	13.3%	14.4%
SR268	Monomer	6.5%	6.4%	6.1%	6.6%
SR368	Monomer	10.6%	10.5%	9.9%	10.7%
SR9003	Monomer				
SR833S	Monomer				
SR399LV	Monomer				
BR952	Oligomer	19.4%	19.1%	18.1%	14.6%
Irgacure 819	Photoinitiator	4.5%	4.4%	4.2%	4.5%
Darocur ITX	Photoinitiator	4.5%	4.4%	4.2%	4.5%
Irgacure 379	Photoinitiator	4.5%	4.4%	4.2%	4.5%
Amide Gellant	Gelator	1.0%	2.5%	7.5%	5.0%
TOTAL		100.0%	100.0%	100.0%	100.0%

Table 10: Ink Formulation with Gellant

<i>Preparation Procedure</i>	A AB6250-1	A and B AB6250-2	A AB6252-1	A AB6252-3	A AB6252-5
Component	Ex.45	Ex.46	Ex.47	Ex.48	Ex.49
SR506A	35.7%	34.6%			
SR272	14.9%	13.8%			
SR268	7.1%	6.0%			
SR368	11.3%	10.1%			5.00%
SR9003			76.50%		
SR833S				76.5%	68.50%
SR399LV			5.00%	5.0%	
BR952	8.0%	8.0%			8.00%
Irgacure 819	6.0%	7.5%	4.5%	4.5%	4.5%
Darocur ITX	6.0%	7.5%	4.5%	4.5%	4.5%
Irgacure 379	6.0%	7.5%	4.5%	4.5%	4.5%
Amide Gellant	5.0%	5.0%	5.0%	5.0%	5.0%
TOTAL	100.0%	100.0%	100.0%	100.0%	100.0%

Claims

1. A dielectric ink composition, comprising:

- at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof;
- a sensitizing photoinitiator;
- an amine synergist photoinitiator;
- a phosphine oxide photoinitiator; and

a gellant.

2. The composition of claim 1, wherein the at least one (meth)acrylate compound includes at least one of the (meth)acrylate oligomers and at least two of the (meth)acrylate monomers, the at least two (meth)acrylate monomers comprising a lowest viscosity mono-functional or di-functional monomer and a highest viscosity mono-functional or di-functional monomer.
3. The composition of claim 2, wherein the at least one (meth)acrylate oligomer is selected from the group consisting of polyester (meth)acrylate oligomers, polyether (meth)acrylate oligomers, epoxy (meth)acrylate oligomers, and urethane (meth)acrylate oligomers.
4. The composition of claim 1, wherein the at least one (meth)acrylate compound comprises at least two different (meth)acrylate monomers, the at least two different (meth)acrylate monomers being selected from the group consisting of monofunctional (meth)acrylates, difunctional (meth)acrylates, trifunctional (meth)acrylates and combinations thereof.
5. The composition of claim 1, wherein the at least one (meth)acrylate compound includes the (meth)acrylate monomers, the (meth)acrylate monomers comprising a trifunctional (meth)acrylate cross linker.
6. The composition of claim 1, wherein the sensitizing photoinitiator is a thioxanthone photoinitiator.
7. The composition of claim 1, wherein the amine synergist photoinitiator is selected from the group consisting of 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one; Ethyl Michler's ketone (EMK) and combinations thereof.
8. The composition of claim 1, wherein the phosphine oxide photoinitiator is selected from the group consisting of Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide; Diphenyl-(2,4,6, Trimethylbenzoyl)phosphine oxide (TPO); Ethyl (2,4,6-trimethylbenzoyl)phenylphosphinate (TPO-L) and combinations thereof.
9. The composition of claim 1, further comprising at least one optional ingredient selected from the group consisting of colorants, polymerization inhibitors, antioxidants and solvents.
10. The composition of claim 1, wherein the gellant is an amide gellant.
11. The composition of claim 10 wherein the amide gellant is an ester-terminated polyamide.
12. The composition of claim 1, wherein the dielectric ink composition has a viscosity ranging from about 2 cps to about 20 cps at 85°C and a viscosity ranging from about 1×10^4 cps to about 1×10^6 cps at 25°C.
13. A method comprising inkjet printing the dielectric ink composition of claim 1.
14. A method comprising aerosol jet printing the dielectric ink composition of claim 1.
15. A device comprising:
 - a substrate;
 - a first conductive line disposed over the substrate;
 - a second conductive line disposed over the first conductive line at a junction; and
 - a dielectric layer disposed at the junction between the first conductive line and the second conductive line so as to electrically insulate the first conductive line from the second conductive line, the dielectric layer being formed by printing a dielectric ink composition, the dielectric ink composition comprising:
 - at least one (meth)acrylate compound selected from the group consisting of (meth)acrylate monomers, (meth)acrylate oligomers and combinations thereof;
 - a sensitizing photoinitiator;
 - an amine synergist photoinitiator;
 - a phosphine oxide photoinitiator; and
 - a gellant.

16. The device of claim 15, wherein the at least one (meth)acrylate compound includes at least one of the (meth)acrylate oligomers and at least two of the (meth)acrylate monomers, the at least two (meth)acrylate monomers comprising a lowest viscosity mono-functional or di-functional monomer and a highest viscosity mono-functional or di-functional monomer.

5

17. The device of claim 15, wherein the sensitizing photoinitiator is a thioxanthone photoinitiator.

18. The device of claim 15, wherein the amine synergist photoinitiator is selected from the group consisting of 2-(4-methylbenzyl)-2-(dimethylamino)-1-(4-morpholinophenyl) butan-1-one; Ethyl Michler's ketone (EMK) and combinations thereof.

10

19. The device of claim 15, wherein the phosphine oxide photoinitiator is selected from the group consisting of Phenyl-bis(2,4,6-trimethylbenzoyl)phosphine oxide; Diphenyl-(2,4,6, Trimethylbenzoyl)phosphine oxide (TPO); Ethyl (2,4,6-trimethylbenzoyl)phenylphosphinate (TPO-L) and combinations thereof.

15

20. The device of claim 15, wherein the gellant is an amide gellant.

20

25

30

35

40

45

50

55

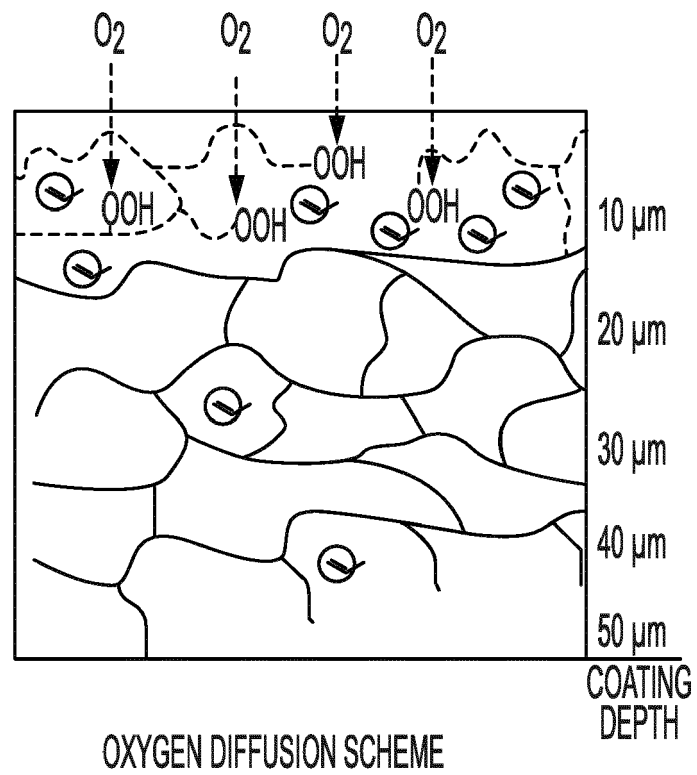


FIG. 1
PRIOR ART

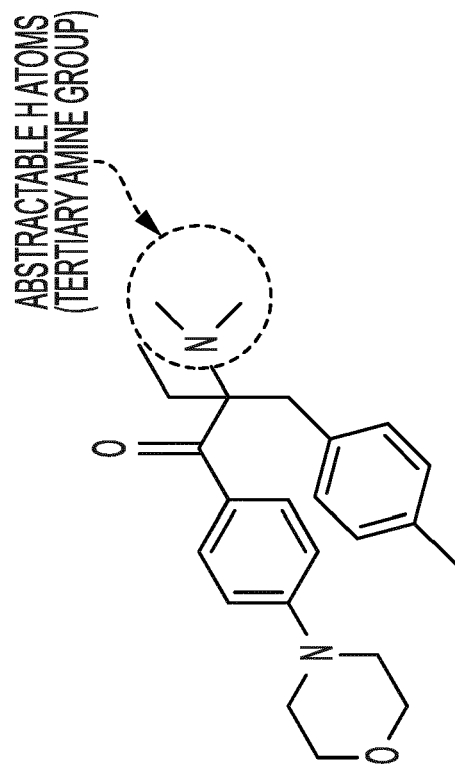


FIG. 2

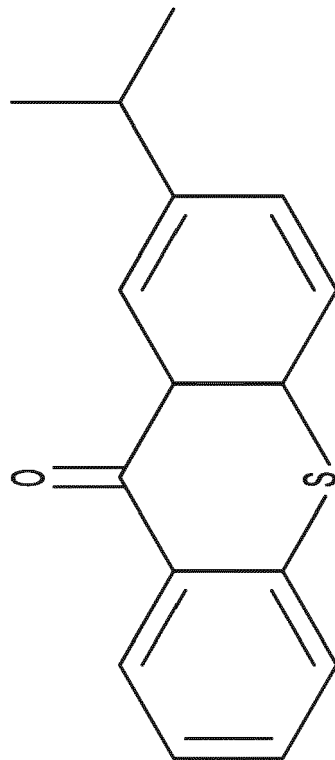


FIG. 3

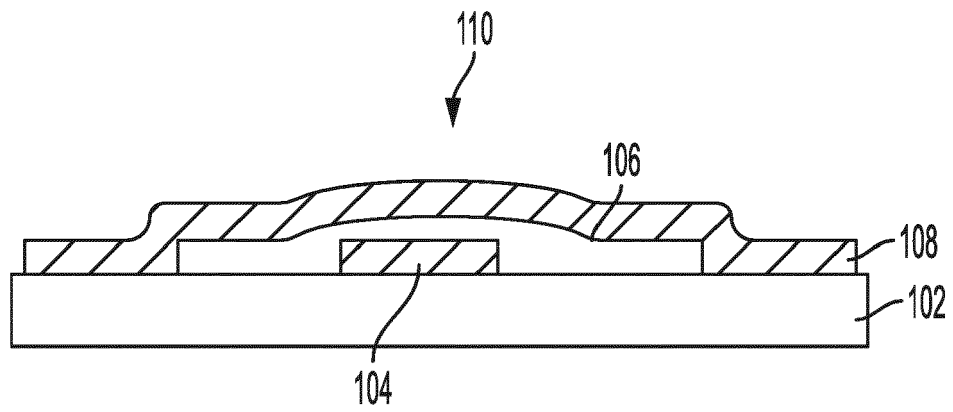


FIG. 4A

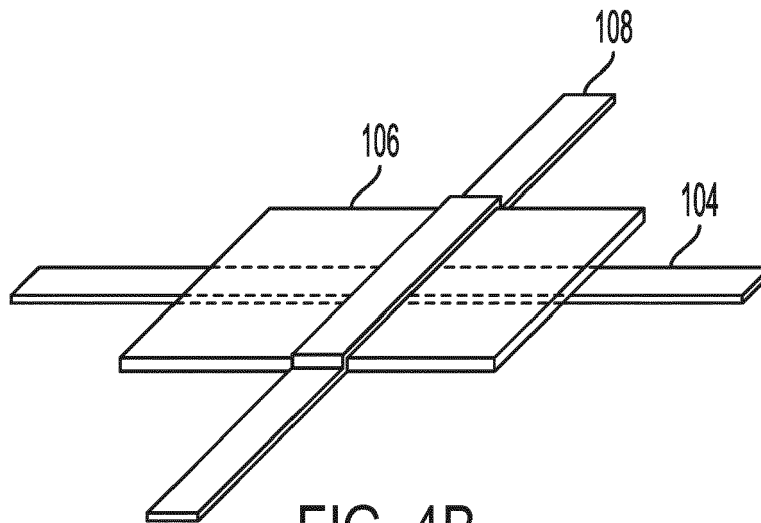


FIG. 4B

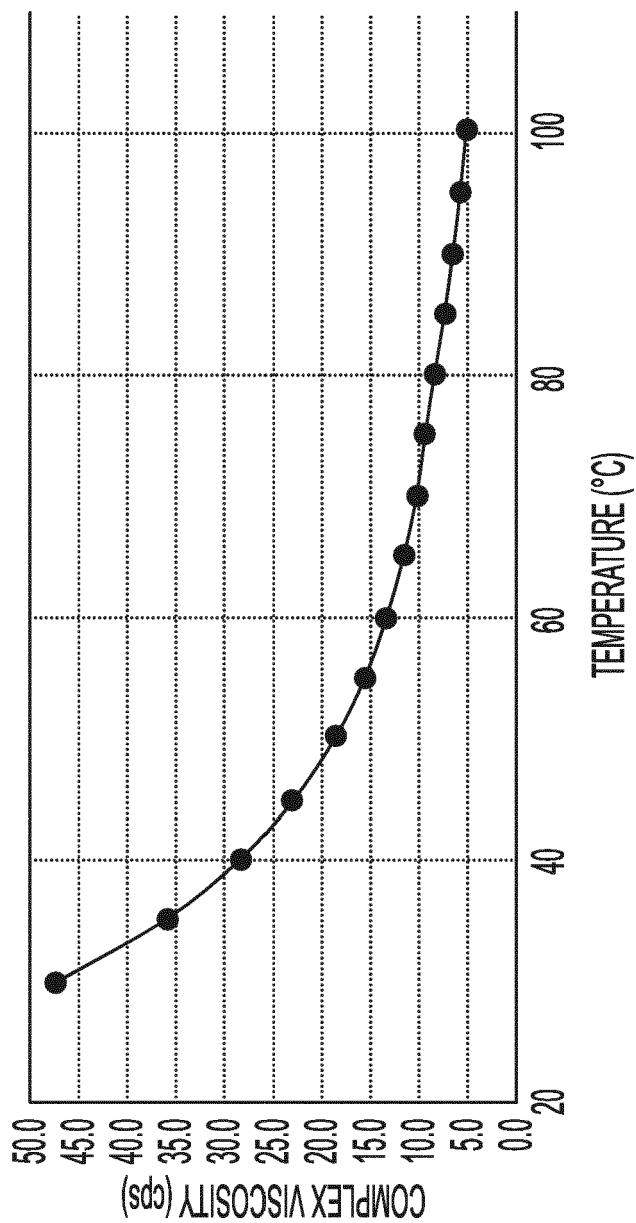


FIG. 5

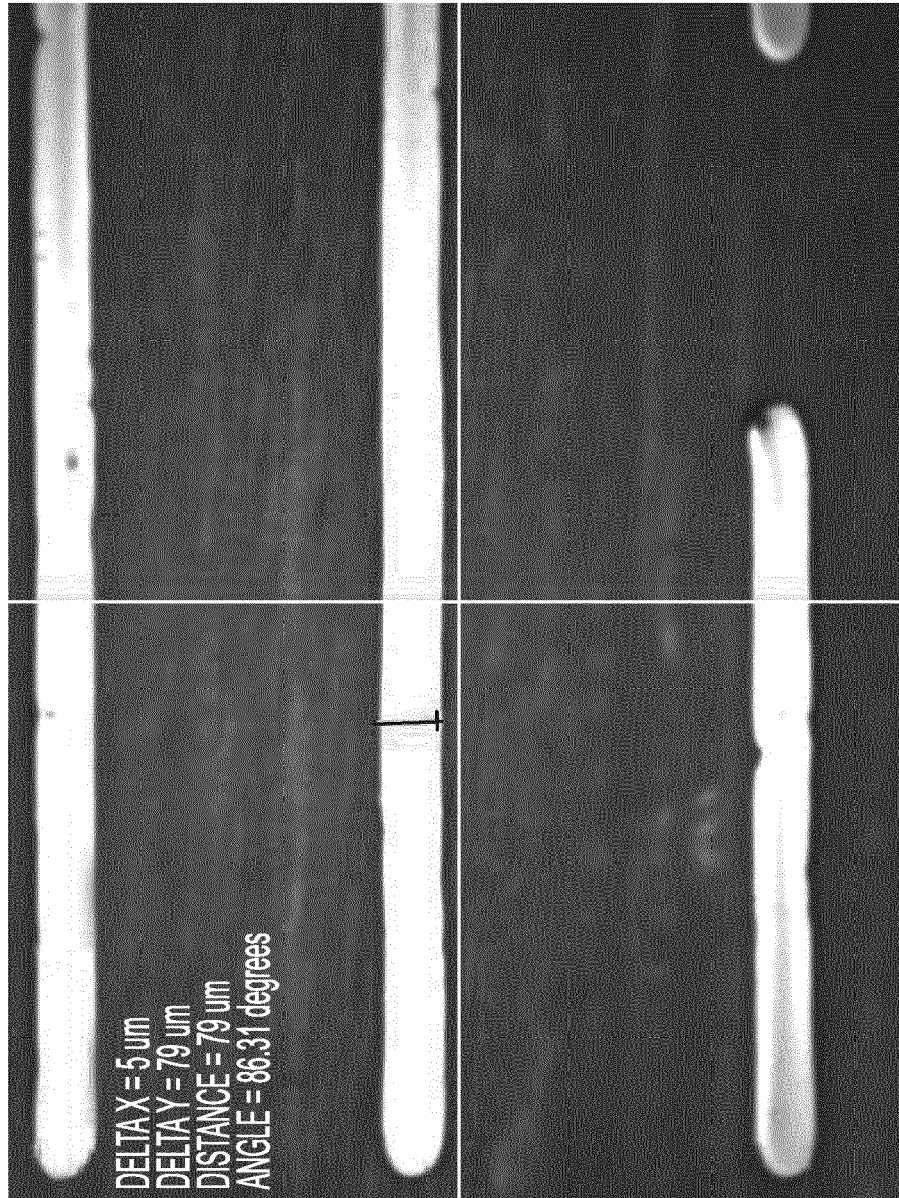
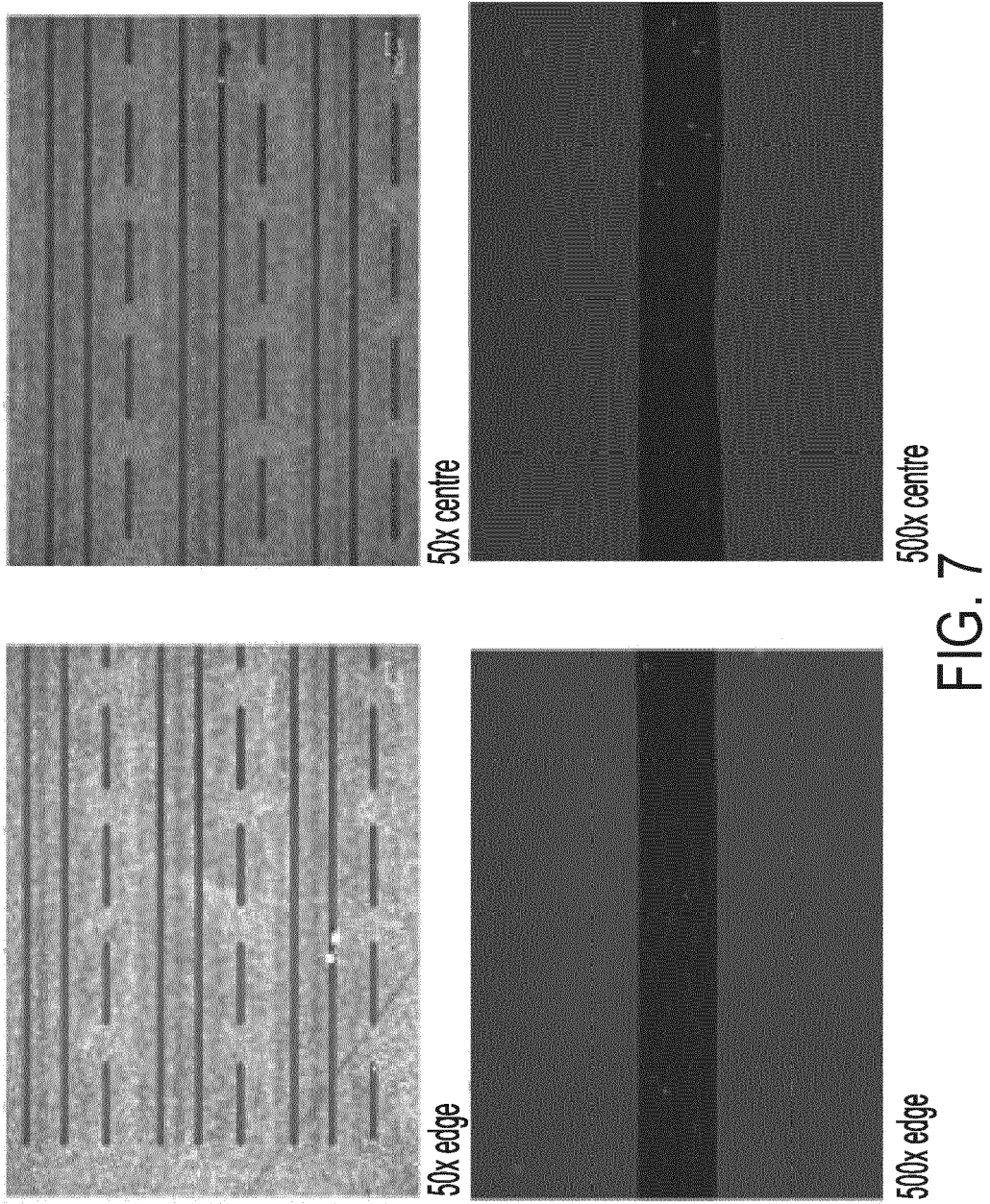


FIG. 6



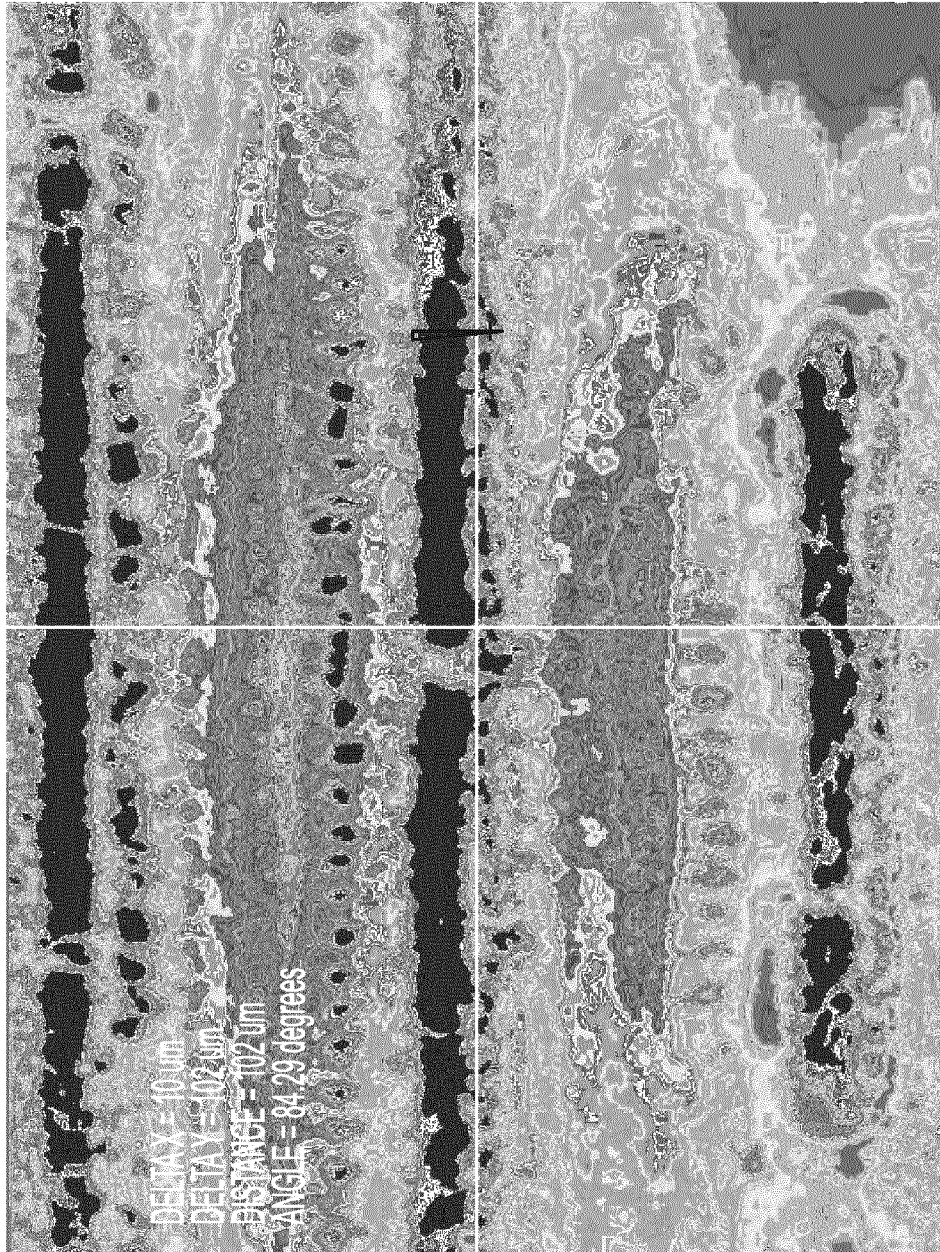


FIG. 8

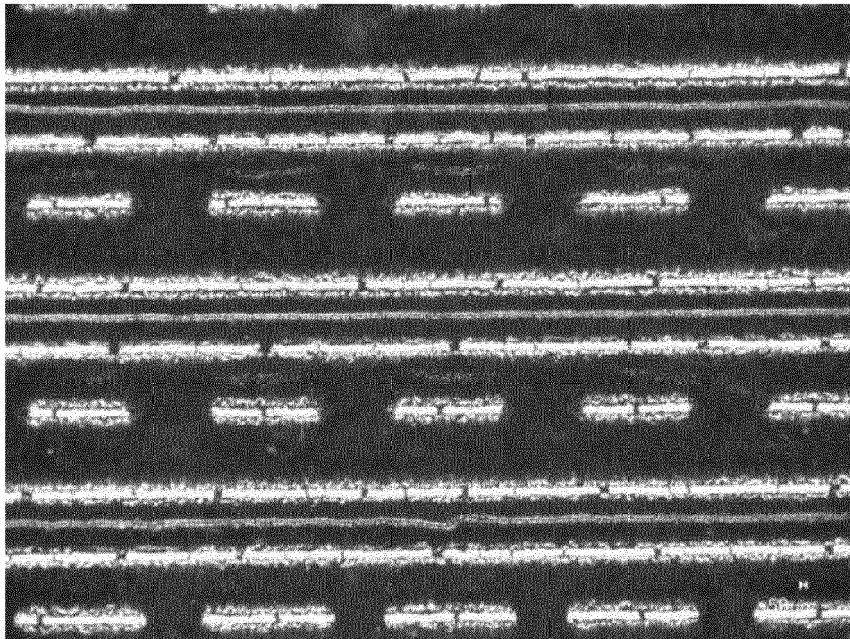


FIG. 9

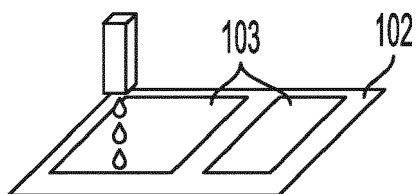


FIG. 10A

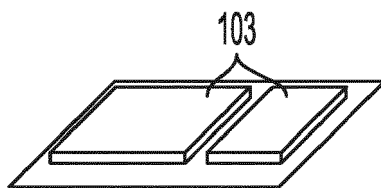


FIG. 10B

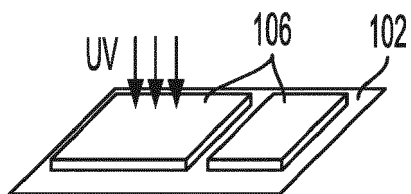


FIG. 10C

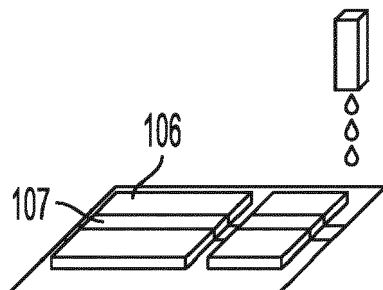


FIG. 10D

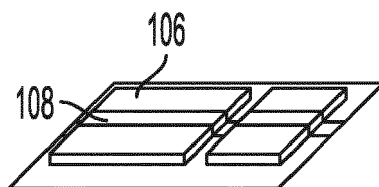


FIG. 10E

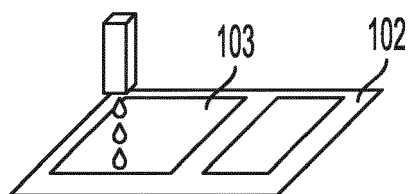


FIG. 11A

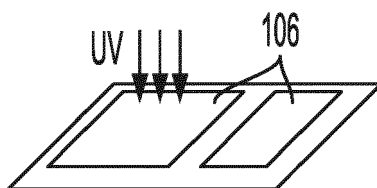


FIG. 11B

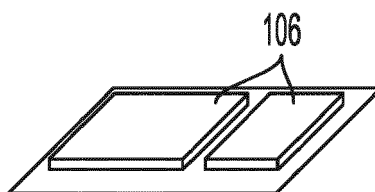


FIG. 11C

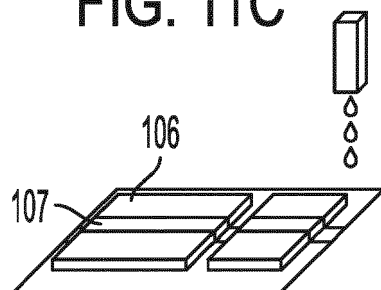


FIG. 11D

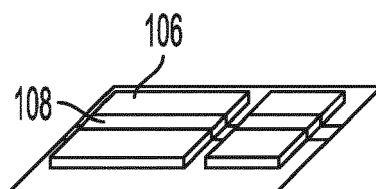


FIG. 11E

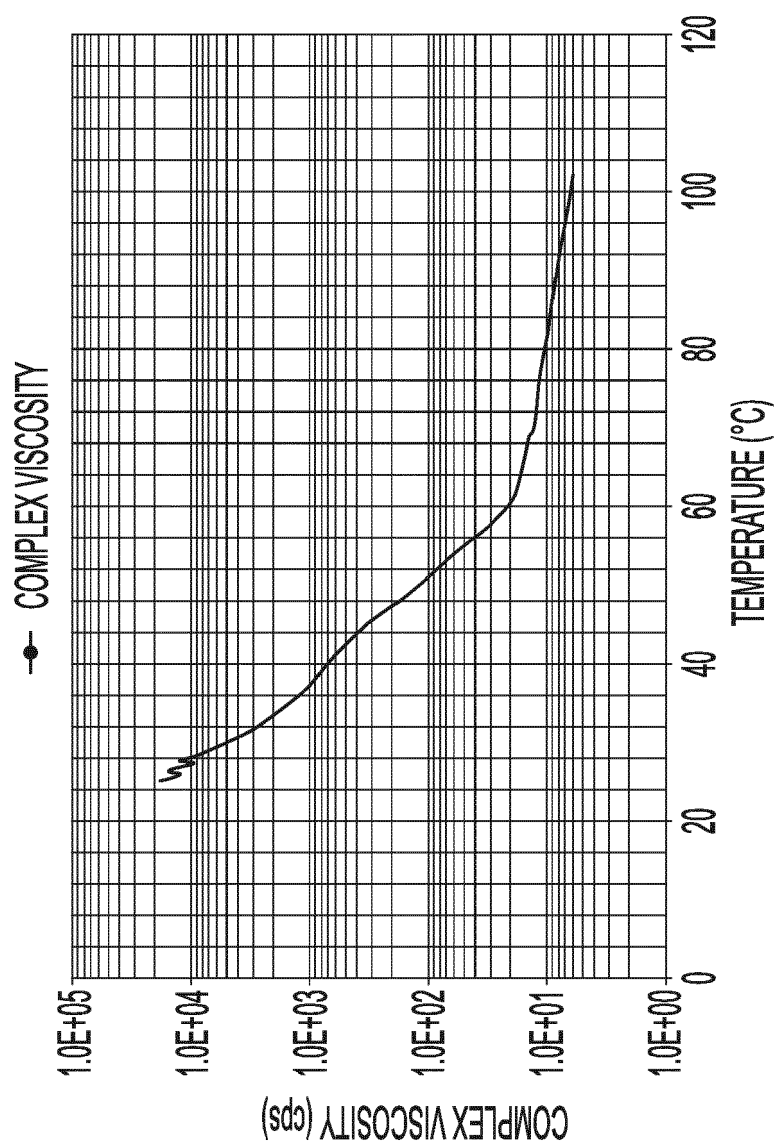


FIG. 12

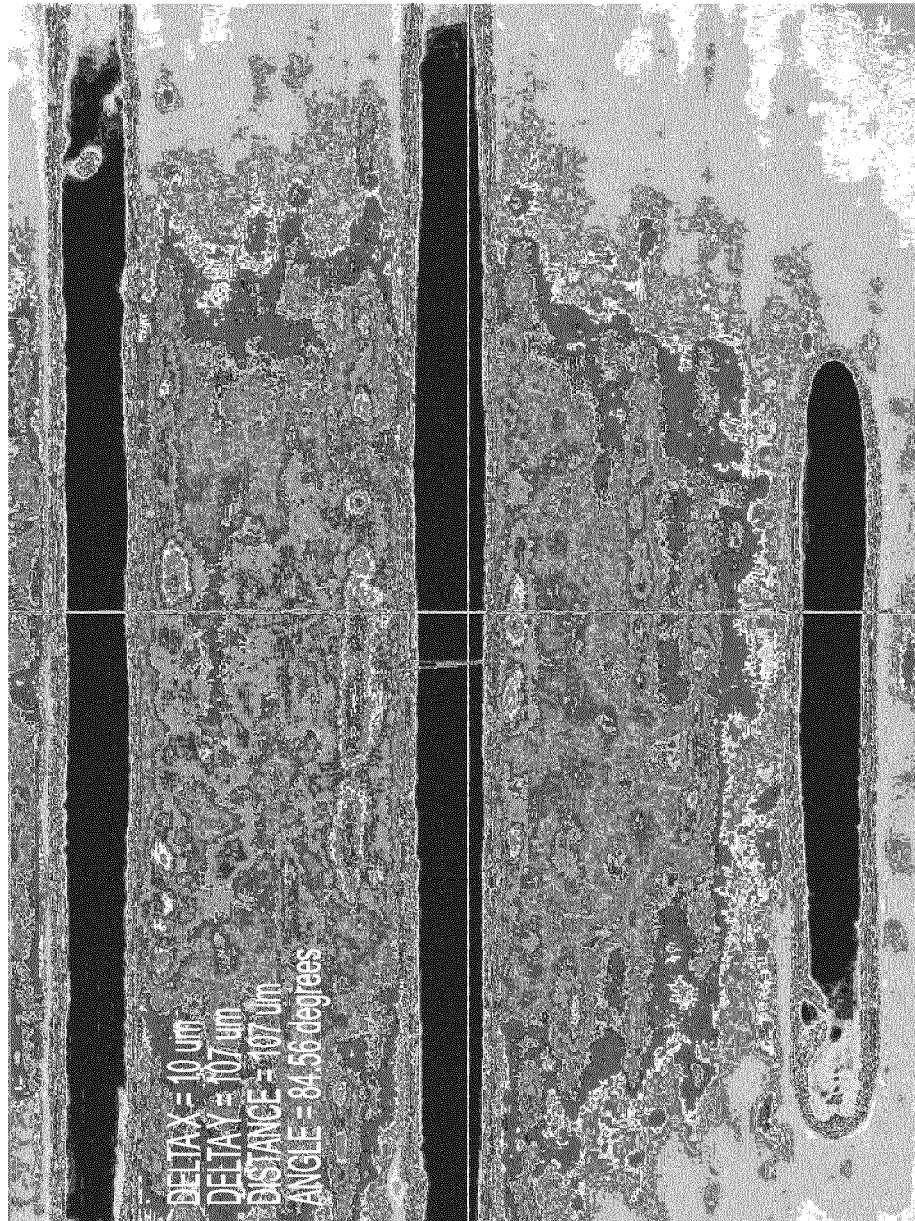


FIG. 13



EUROPEAN SEARCH REPORT

Application Number
EP 19 20 0662

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 9 016 847 B1 (KONICA MINOLTA INC [JP]) 28 April 2015 (2015-04-28)	1-6, 8-10, 12-14 15-20	INV. C09D11/101 C09D11/38
Y	* the whole document * * claim 4; examples 4-5; table 1 *		
X	US 9 458 335 B1 (SLOAN DONALD D [US]) 4 October 2016 (2016-10-04)	1-6, 8-10,12 15-20	
Y	* the whole document * * column 6, line 8 - line 20; examples; tables 1,2 *		
X	US 2010/323102 A1 (CHOPRA NAVEEN [CA] ET AL) 23 December 2010 (2010-12-23)	1,4,6-14	
Y	* the whole document * * paragraph [0122]; claim 2 * * paragraph [0138] - paragraph [0139]; example 2 * * paragraph [0105] *	15-20	
Y	WO 2018/136480 A1 (SUN CHEMICAL CORP [US]) 26 July 2018 (2018-07-26)	15-20	TECHNICAL FIELDS SEARCHED (IPC)
	* the whole document * * paragraph [00013] - paragraph [00018] * * paragraph [00032] * * paragraph [00067] *		C09D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 19 February 2020	Examiner Rangheard, Claudine
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 19 20 0662

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-02-2020

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 9016847	B1	28-04-2015	EP 2840119 A1	25-02-2015
			JP 5991371 B2	14-09-2016
			JP WO2013157271 A1	21-12-2015
			US 9016847 B1	28-04-2015
			WO 2013157271 A1	24-10-2013

US 9458335	B1	04-10-2016	US 9458335 B1	04-10-2016
			WO 2017004198 A1	05-01-2017

US 2010323102	A1	23-12-2010	CA 2708056 A1	23-12-2010
			CN 101932201 A	29-12-2010
			EP 2267478 A2	29-12-2010
			JP 2011009743 A	13-01-2011
			KR 20100138799 A	31-12-2010
			US 2010323102 A1	23-12-2010

WO 2018136480	A1	26-07-2018	CN 110520488 A	29-11-2019
			EP 3571253 A1	27-11-2019
			WO 2018136480 A1	26-07-2018
